

Annual Technical Report

from

Charles Evans and Associates
1670 South Amphlett Blvd. Suite #120
San Mateo, CA 94402
(415) 572-1601

Investigation and Development
of Advanced Surface Microanalysis
Techniques and Methods

sponsored by:

Defense Advanced Research Projects Agency (DOD)

DARPA Order #4713

Under Contract #MDA903-83-C-0099 by Department of the Army
Defense Supply Service-Washington, DC 20310

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION IS UNLIMITED (A)

Co-Investigators:

Dr. Robert W. Odom
Project Scientist

Dr. Charles A. Evans, Jr.
President

CLEARED

FOR OPEN PUBLICATION

AUG 7 1984 21

DIRECTORATE FOR FREEDOM OF INFORMATION
AND SECURITY REVIEW (OASD-FSI)
DEPARTMENT OF DEFENSE

Effective Date: April 1, 1983

Expiration Date: April 1, 1985

Reporting Period: April 1, 1983 - March 30, 1984

"The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government."

84 08 09 097 02

AD-A144 166

DTIC
ELECTE
AUG 10 1984

A

Investigation and Development of Advanced Surface Microanalysis
Techniques and Methods

INTRODUCTION

The successful development of advanced materials systems and devices depends strongly on sensitive quantitative materials characterization provided by surface microanalytical techniques. At the present time, the materials systems under development or envisioned for the near future are at or beyond the capabilities of state-of-the-art materials characterization techniques and methodologies. If these new materials development programs are to be successful, a parallel effort to advance existing microanalytical techniques and develop next generation capabilities must be initiated.

This two year research program, performed by CHARLES EVANS AND ASSOCIATES, is directed toward the advancement of the performance capabilities of surface microanalytical techniques in order to meet the current or near term, as well as future materials characterization demands of advance materials development programs. The goals of this research program are two fold:

- 1. Improve the sensitivity and quantitative capabilities of existing surface microanalysis techniques operating in the 1-50 microns lateral dimension regime, and
- 2. Investigate and evaluate techniques for obtaining trace level analyses of materials down to the 1/10 micrometer lateral dimensions.

Successful achievement of these two goals will insure that surface and microanalysis continues to provide the necessary characterization for advanced materials development.

REPORT

This research program is divided into two distinct phases. The first phase is concerned with improving the sensitivity and quantitative performance of existing state-of-the-art surface analysis techniques, while the second phase will determine the feasibility of advancing surface microanalysis to sub micron lateral resolutions while maintaining trace level detection sensitivities. During the performance of this research, additional analytical needs have come to our attention. These include:

1. Improved depth profiling techniques which will provide a more sensitive analysis of the outermost surface,
2. Improved depth resolution for heterostructures and superlattice type systems, and
3. An ever increasing need for improved bulk analytical techniques which will provide sensitivities and quantitation to meet the demands of the crystal growth community and the users of semiconductor materials. The technologies requiring improved bulk analysis range from the existing silicon industry through to the more advanced electro-optical materials for infrared imaging (HgCdTe) and bismuth silicon oxide and the photo refractive materials being investigated at the University of Southern California.

I. Improving the Sensitivity and Quantitation of Existing Surface Analysis Techniques

During the first year of this program we have performed studies in three areas which, if successful, will improve either sensitivity or quantitation of existing state-of-the-art microanalytical techniques. For the purposes of this study, the three techniques involved are Rutherford Backscattering Spectrometry (RBS), Scanning Auger Microscopy (SAM), Secondary Ion Microanalysis or Secondary Ion Mass Spectrometry (SIMS). The three areas studied have included:

1. Developing methods for improved quantitation of the two microanalytical techniques (SAM and SIMS),
2. Investigations into improving the sensitivity of Secondary Ion Mass Spectrometry for the microanalysis of 10-50 micrometer diameter areas, and
3. Developing methods for extending quantitative SIMS ion microanalysis down to improved lateral resolutions.

One of the major limitations of present surface microanalytical techniques, especially scanning Auger microscopy and SIMS/ion microanalysis, is the lack of suitable standards for the materials of current interest. Standards are required for calculating component concentrations from the intensities of the analytical signals produced by these two techniques. As with any analytical technique, one must find a method whereby a material of a known composition is analyzed and the conversion factor derived to convert the arbitrary analytical

signal into concentration. The most demanding requirement is that in almost every analytical technique the standard and the unknown must have very similar or identical compositions at the major constituent levels (i.e., matrix). That is to say, if one wishes to analyze boron in silicon or boron in phosphosilicate glasses (PSG) then the standard containing the known amount of boron must be either silicon or a phosphosilicate glass. It is insufficient to know the conversion factor for boron in GaAs for the silicon or phosphosilicate glass samples. At the impurity level, ion implantation can be used to create a standard of X in a matrix of Y for a SIMS analysis. However, whenever analyzing at the major and minor constituent levels there are serious complicating factors. Of course the preparation of a standard by implantation at the percent level is time consuming. By the nature of trying to perform a compositional analysis at a major constituent level (e.g. the tungsten content of a tungsten silicide or the boron concentration of a borophosphosilicate glass) the preparation of a standard with major constituent composition identical to the unknown implies an understanding of the unknown that obviates the need to perform the analysis! Unfortunately, analysis at the major constituent level is of serious technological interest since the composition of metal silicides, borophosphosilicate glasses (BPSG), etc., dramatically influence the final electrical properties of a device. These materials also provide the most demanding analytical situation for any of these techniques due to the nature of the analysis and the highly defined geometries encountered in real devices. Thus, we have investigated the possibility of using techniques which are quantitative at the major constituent level to prepare standards which can then be used as standards by the microanalytical techniques. Such is the case for the characterization of boron and phosphorus in borophosphosilicate glasses (of current technological interest) or for the characterization of refractory metal silicides whether deposited by CVD or sputter techniques.

The first of these studies was that of boron and phosphorus in borophosphosilicate glasses. Due to spectral interference problems we were unable to use the absolute quantitative capabilities of the Rutherford Backscattering technique and had to turn to the use of wet chemistry and electron microprobe analysis. These techniques are capable of providing a quantitative analysis of a thin film, with little regard for either lateral or in-depth considerations. In this case, we obtained a series of borophosphosilicate glasses containing varying amounts of boron, phosphorus and silicon and submitted them for analysis by one of these large area (conventional wet chemistry) or non-profiling techniques (electron microprobe). Electron microprobe analyses were performed on the series of samples containing only phosphorus. Boron and phosphorus analyses were performed by wet chemistry on another set of samples in order to obtain the best possible cross correlation. These samples were then analyzed by

secondary ion mass spectrometry to obtain the in-depth intensities of boron, phosphorus, silicon and oxygen. The first set of samples analyzed were five samples of phosphosilicate glass produced by conventional CVD deposition of the overlayer. In this particular set of samples the analyses were then analyzed by electron microprobe and appropriate quantitative correction procedures obtained. In order to perform a proper quantitative SIMS analysis we had to monitor not only the unknown constituent intensities, phosphorus in this case, but we are required by the nature of the SIMS technique to monitor a species of constant composition so as to provide a correction for sample-to-sample variations in set-up or other analytical conditions. Thus, if one plots the analytical signal of interest, (phosphorus divided by silicon) versus the phosphorus content by electron microprobe (Figure 1) we see that there is a non-linear relationship. Although smoothly varying, the phosphorus to silicon intensity ratio is not linear as is desired for a quantitative analysis. This non-linearity is due to the fact that as we add phosphorus during the deposition it is substituting for the silicon, thereby silicon is not remaining constant, and the phosphorus-to-silicon ratio is increasing non-linearly as we add phosphorus. Thus it is necessary to actually compare the phosphorus-to-silicon ratio as determined in the SIMS with that ratio determined by electron microprobe (Figure 2) in order to obtain a linear relationship. In this case, we see one of the true values of the SIMS technique when operating at the major constituent levels. Although there are these complicating effects of matrix, etc. which continually plague the technique, if proper quantitative procedures are employed, the ion intensities are so large (greater than 10^6 counts a second) that "root n" statistics and other random variations are sufficiently small that a very linear quantitative relationship can be obtained between the analytical ion signals and the known, quantitative concentration.

It is interesting to note that this ability to analyze at the major constituent level is generally associated with electron spectrometry not SIMS. However, analysis of these samples by Auger electron spectrometry gave poor results due to the inability of the conventional Auger configuration to cope with the serious surface charging effects obtained when performing a charged particle analysis of such a dielectric sample.

With the successes obtained on this single-element doping, three component system (P, Si, O) we progressed to borophosphosilicate glasses which are of great interest to current semiconductor technology due to their improved reflow characteristics and the ability to provide softening point suppression with the boron as well as the phosphorus. In this way one can produce a softenable glass (doped with boron) next to the aluminum rather than having phosphorus bearing glass next to the aluminum. Poor phosphorus control routinely leads to aluminum corrosion. Thus, by depositing boron doped glass

next to the aluminum followed by a phospho- or borophosphosilicate glass, the potential for corrosion can be reduced, reflow characteristics can be maintained and gettering of ion contaminants performed by the phosphorus. Samples of LPCVD BPSG layers were characterized by wet chemistry for their boron and phosphorus content. Boron can not be detected by Rutherford Backscattering nor the electron microprobe, and the films were sufficiently thin that the electron microprobe sampling depth was greater than the film thickness. Profiling these samples by SIMS determined that there are zones or layers in the sample containing varying compositions of boron and phosphorus (Figure 3). At first it would seem difficult to actually use these samples as quantitative standards given their inhomogeneity with depth. However, quantitative analysis using wet chemistry to remove the entire layer and analyze its content is much like calibration using an ion implant. In this case we know the total boron and phosphorus content of the films from the wet chemistry since the entire film is dissolved away for the wet chemical analysis. Similarly, we know the total integrated boron, phosphorus and silicon SIMS intensities for the total number of boron and phosphorus atoms. Thus, we can set integrated intensities equal to the total atom concentration and determine a sensitivity factor which will allow quantitation of the SIMS ion intensity profiles (Figure 4).

A variety of procedures were required to convert the logarithmic ion intensities into quantitative concentration versus depth profiles. First, we had to obtain the linear relation between the boron and phosphorus content and the secondary ion signals shown in Figures 5 and 6. Next we had to use a normalization technique to compensate for the severe surface charging encountered with these samples. Not only were we required to use gold coating to conduct away surface charge, but we also had to use electron beam neutralization in order to reduce the surface charge to an analytically acceptable level. The effect of the surface charging can be seen in Figure 3, not only in the low intensities near the surface and the higher ion intensities in the interior of the material but also by observing the variations in the dotted line, called the charging curve. Even though all of the above charge reduction techniques were employed, there was still charging of the surface of the sample which was then compensated by using a voltage offset technique. We then employ software to show the extent of surface charging along with the ion intensity in order to correlate any anomalies in ion intensity with any major or minor change in the surface charging. Normalization of the boron and phosphorus signals to the silicon intensity gives a normalization which reduces the effect of charging on intensity and permits the correction of ion intensity (Figure 3) into a quantitative depth profile (Figure 4). The thickness of the film was determined using surface profilometry after the analysis in order to convert sputtering time into depth.

An interesting aside is the understanding that the boron and phosphorus intensities were modulated rather than being uniform throughout the film as was proposed by the preparer of the samples. If one examines a schematic of the LPCVD deposition system as in Figure 7, we see that there are three zones where the reactants enter into the deposition system and four zones where the reactants and reaction products escape. Thus, the three zones of high concentrations and the four zones of low concentration noted in the SIMS profiles can be correlated directly with the geometry of the deposition system. With this information one can iterate on the design and operating conditions of the deposition system to now provide the tailored concentration profiles that are required of the use of this evolving technology.

We feel that this detailed study of BPSG compositional analysis is illustrative of the capabilities of deploying the microanalytical techniques of SIMS (and presumably Auger) at the major and minor constituent levels, given that sufficiently quantitative samples are provided as standards for the subsequent quantitative analysis of unknowns. To this end, we are going to now evaluate the use of Rutherford Backscattering which can provide accurate quantitative analyses on metal silicide systems, another evolving technology, to develop standards which can then be used for the quantitative microanalysis using either SIMS or scanning Auger microscopy. We feel with that demonstration of capability that we will have completed the goals of this particular part of the contract.

The next area of investigation dealt with improvements in the quantitative detection sensitivity of secondary ion microanalysis over conventional lateral dimensions of 20 to 150 micrometers. The improvement in the detection sensitivity of this, as well any analytical technique, can be accomplished by:

1. increasing the analytical signal, (secondary ion yields in this case), or
2. by reducing background noise or spectral interferences produced either by the electronics involved or the spectral features inherent in the technique.

Thus, one is enhancing the signal-to-noise ratio in order to obtain a better detection limit. In the case of secondary ion mass spectrometry, electronic noise is not a problem. Therefore, we must focus on the discrete background, spectral interferences, for this purpose. As described above, two approaches can be made to improve the detection limits or the signal-to-background. One is to focus on those elements which exhibit poor secondary ion yields. These elements include species such as cadmium and zinc which are used in GaAs

device fabrication and InP fabrication, as well as the analysis of mercury in HgCdTe. Even though the mercury content of HgCdTe may be very high, one needs as much signal as possible to provide major constituent diffusional information.

The most common background interferences encountered in SIMS limiting detection sensitivity are molecular ion interferences which occur at the same nominal mass as the atomic ion of interest. Common examples of molecular ion interferences are:

1. 30SiH providing an interference at 31P in silicon matrices,
2. Si_2O producing an interference at 75As ,
3. CO and N_2 causing an interference for Si analyses in GaAs, and
4. CdH causing an interference with the major isotope of In in CdTe or HgCdTe.

For sake of this discussion, we will deal for the moment only with activities dealing directly with the improvement of existing SIMS instrumentation. It should be noted that there are a variety of evolving techniques which may cause either signal improvement for secondary ion mass spectrometry or reduced spectral interferences in secondary ion mass spectrometry. These will be discussed later under the "Evaluation of Evolving Techniques" section.

The enhancement of ion yields requires that some process be used to increase the probability of the conversion of a sputtered neutral atom into either a positive or negative ion. In state of the art secondary ion mass spectrometry instruments this is accomplished by using oxygen ion bombardment to enhance positive ion emission (i.e. electron detachment from the departing atom) or cesium ion bombardment in order to enhance negative ion formation (the attachment of electrons to the departing atom). If one was to pursue this concept further, the use of either more electronegative or electropositive species for the oxygen or cesium ions could be envisioned. However, in the past, those who have tried species such as fluorine have encountered serious difficulties because fluorine attacks the components of the secondary ion mass spectrometer. The severity of the deleterious instrumental effects do not warrant expending further efforts in this direction. Given that the lowest IP element is presently being used (i.e. cesium) to enhance the electron transfer process, we can envision no other methods for improving negative ion formation. Thus one must turn to some sort of auxiliary ionization technique such as electron impact or photo ionization using a laser.

We know from historical data that electron impact is insufficient to give

enhancement over and above that of the use of reactive ion bombardment, thus we are left with the use of laser irradiation for positive ion enhancement by the use of energetic photons to bring about electron ejection from the departing atom. This process requires that the impacting photon be of an energy greater than the ionization potential of the atom to be ionized or that multiple photons arrive within a sufficiently short time that one promotes the electron of the atom to an intermediate state, followed by absorption of the other photon, to be followed by ionization. This process may require two, three or more photons. Alternatively, the atom can be in a metastable state, part way between the ground state and a fully ionized state such that the incoming photon brings about the ionization event.

Given the need for a single photon to have an energy in excess of the atom ionization potential for single photon ionization, we can readily see that only three elements, cesium, rubidium and potassium can be ionized with conventional lasers, and these must all be in the UV. However, if a pulsed laser is used we can provide a sufficiently high photon flux that two or more photons can be in the same position in the space-time continuum to bring about multiphoton ionization of a single atom. Unfortunately, the use of pulsed lasers is not compatible with conventional secondary ion mass spectrometry due to the need for a CW rather than pulsed signal, in order to realize the overall enhancement efficiencies. Given that we need a DC, photo enhancement process for conventional SIMS, we turn to the situation wherein the atom of interest must be present in an intermediate metastable state from which we could ionize. The most obvious candidate, given the data we had at hand, was Hg sputtered from HgCdTe. We had observed that, contrary to the observations made for all of the other secondary ions, Hg exhibited a very large number of ions with kinetic energies less than that which would be imposed on the atom due to the sample accelerating potential. Hence, we know that the ions are being created in the gas phase by one or more of several potential mechanisms. One is that the atoms are sputtered in a metastable state and de-excite due to the emission of an electron, or the atoms are produced by gas phase collisional processes. Given the metastable energy diagram of Hg, we surmised that it might be possible to bring about enhanced decomposition in the gas phase of sputtered Hg atoms, if they were present as metastables, with the light produced from a CW Ar ion laser.

For this experiment we then modified the IMS-3f Ion Microanalyzer so as to admit light of the appropriate energy as well as modified the mass spectrometer to accommodate to the energies produced in that part of the sample potential field which was irradiated by the laser. After a variety of experiments, scanning over a very broad energy, we were unable to detect any enhancement of the mercury ion intensity using the laser excitation. Although these results are negative for the experiment we wished to accomplish, they

did indicate that another potential mechanism was operative. Given that this understanding of the mechanism was germane to the analysis and characterization of HgCdTe, we then pursued an understanding of this process with funds available under another contract. The results have been reported therein and can be summarized as most mercury ions came about as a result of collisions between the sputtered Hg atoms and the incoming primary ions. The results of this study indicate that if we are to accomplish any enhancement of the ionization process via photo ionization processes, we must turn to much higher power density lasers with wave lengths in the ultraviolet necessitating the use of pulsed ion beams, pulsed lasers and concomitant mass spectrometry. These processes will be addressed later under "Evolving Techniques."

The alternative method of improving signal-to-noise in conventional SIMS, and hence sensitivity, is to reduce the background signals provided by molecular ions produced during the sputtering process. We have proposed three methods for the reduction of these molecular ions.

1. The first is specific to negative ion spectroscopy wherein we would use the photo-detachment process in order to selectively detach electrons that are attached to molecular ions interfering with a specific atomic ion.
2. The second proposed approach would apply to both positive and negative ion spectroscopy and would use the laser photons to dissociate molecules, either positively or negatively charged, in flight.
3. The third method would use predissociation techniques wherein laser light was used to selectively pump one of the components of the molecular ion into a disassociative state during the sputtering process.

All three of these processes require that we be able to irradiate the sample normal to the surface or to actually bathe the ion beam in flight with laser light. To this end, we designed and obtained a special electrostatic analyzer which would allow us to pass the laser light through the electrostatic analyzer so that the desired charged particles would be deflected while the now neutralized ions would not be deflected. This electrostatic analyzer has been tested, and we find that it does not disturb the ion imaging mode but does adversely affect one of the modes of SIMS analysis known as high mass resolution. We are now in the process of electrostatically shimming the hole produced in this electrostatic plate so that the instrument would be useable in all modes of analysis.

A highly different technique for increasing the detection sensitivity of SIMS analysis is based on a technology developed by Dr. Kenneth Purser, Theodore

Litherland and Harry Gove and is referred to as "ultra sensitive SIMS" or "accelerator based SIMS." This technique employs negative secondary ions sputtered from the sample surface which are then accelerated into a tandem accelerator with its terminal held in the range of one to two megavolts. When the negatively charged, highly energetic atomic and molecular ions reach the terminal they pass through a stripper gas or stripper foil which removes electrons and dissociates any and all molecular species present in this ion beam. Now the positive atomic species, those originally present as atoms as well as those from dissociated molecules, are accelerated from the positive terminal, mass separated and detected.

We are presently preparing for a series of experiments to evaluate this technique for removing the molecular ions which plague our efforts to improve the sensitivity of conventional SIMS. For the study we are employing an instrument in the Department of Geology at the University of Toronto. (None of these instruments are available in the U.S.) At the moment this technique cannot truly be designated microanalytical, but we are investigating the viability of accelerator based SIMS for the trace element analysis of bulk materials in order to determine if this technique will have an impact on semiconductor materials technology. The samples have been collected for this study and time has been allotted to us by the staff at the University of Toronto. The first sample set consists of samples of Si doped with known concentrations of B, P, As and Sb, the common dopants in Si, as well as samples of Si containing undesirable impurities of the transition elements (in particular, Fe) at known concentrations. By using these samples containing known concentrations we can determine the sensitivity factors or the conversion factors required to establish the intensity to concentration correction, for the quantitation required to determine the ultimate sensitivity of the technique. Once we have determined these sensitivity factors, we then have ultra-high purity float zone Si provided by a collaborator at Monsanto which will allow the measurement of the signals in undoped material thereby determining the extent of sensitivity gain that can be realized through this technique. We very carefully have chosen the elements for this study:

1. Boron represents an element quite sensitive by conventional SIMS and exhibits no spectral interference problems. Thus, we can see if the required use of cesium ion bombardment and negative ion spectroscopy combined with the complex ion optics used for such an analysis actually degrade the analysis which can be provided by conventional SIMS
2. Phosphorus has been chosen because there is an interference consisting of a simple molecule of Si and H.

3. Antimony has been chosen because the interfering molecule is quite complex, Si_2O .

4. The Fe is of exceeding importance in semiconductor grade Si since Si is commonly made from starting material containing high concentration of Fe. The spectral interference which prevents conventional SIMS from measuring Fe below 1×10^{16} at/cm³ is very intense.

Once we have established the nature and value of the technique in silicon we will then progress to materials technologies such as GaAs and HgCdTe. We would hope by the time of the next report to have obtained data on the Si based study.

II. Extending Quantitative Sims Ion Microanalysis Down to 1-10 Micrometer Lateral Dimensions

Although the enhancements in trace level detection sensitivity of SIMS discussed above are appropriate for lateral resolutions greater than 10 micrometers, the need to perform quantitative trace level analysis at lateral resolutions significantly less than this are currently required for direct device applications. Although conventional SIMS instrumentation has image resolutions of better than 1 micron, the instruments can not really perform an analysis in small areas due to the nature of the ion optics. Some years ago, under the auspices of other contracts, we began the development of instrumentation which will allow us to perform digital image processing either using camera based digital image processing or using a device known as a resistive anode encoder. These two programs are presently being funded by the Air Force and the National Science Foundation, respectively, and we only include comments on them in this report for completeness since these programs will indeed impact the overall level of improvement that can be achieved with the microanalytical techniques. At the present time we are not pursuing any research in these areas under this contract.

III. Investigation of Techniques For Achieving Trace Level Detection Sensitivities at 0.1 Micrometer Lateral Resolution

The future demands for trace level sensitivity in advanced electronic devices requires surface microanalysis capabilities which can not be achieved by present day SIMS/ion microanalysis. In fact, these demands will not be completely met even if the detection sensitivity enhancements discussed in the previous section are accomplished. The fundamental limitations of the SIMS technique is illustrated by examining the requirements of ppm detection sensitivities with a 0.1 micrometer lateral resolution and at a 100 Angstrom

depth resolution. Even with an optimized SIMS assuming 50% ionization and 10% mass spectrometer transmission, not even one single count would be produced from this volume for a ppm (5×10^{16}) component. It is apparent from this observation that what is required in order to achieve a detectable signal at this concentration is total ionization and mass analysis transmission efficiencies approaching 100%. Thus, we are lead to the conclusion that new analytical techniques must be developed and evaluated if we are to realize the sensitivity and detection limits required for future device geometries.

During this study of new microanalytical techniques and discussions with material scientists, device engineers and crystal growers, it became apparent that even before one must worry about lateral microanalysis with 0.1 micron or so resolutions, there must be improvements made in the ability to perform bulk and depth profiling analyses.

1. There is a continuing need in present semiconductor technologies, particularly those using Si for more sensitive, surface specific analysis to examine a breadth of surface contaminants as a result of surface preparation and cleaning procedures.
2. There is a need for improved depth profiling capabilities with better depth resolution. Improvement is required for a host of technologies in silicon, as well as for devices being fabricated from III-V and II-VI compound semiconductors, wherein very thin layers are used as active layers, or superlattice structures are used to provide the necessary electrical performance.
3. There is a need for more sensitive analysis at the bulk impurity level. Silicon crystal growth technology is still plagued by unintentional impurities as is GaAs, InP, CdTe and HgCdTe. The new materials are highly non-conducting thereby confounding most of the sensitive, bulk analytical techniques, yet need trace element analyses at the 0.1 to 1000 ppm levels.

Thus research for achieving better detection sensitivity can really be broken down into two studies. One is the achievement of improved capabilities for in-depth and bulk analysis with little or no regard for lateral resolutions as long as 0.1 mm to 1 mm resolutions are provided. The second is the need for an improvement in the overall efficiency of signal generation and collection to accompany sub-micron analyses. Thus, it became incumbent upon us to investigate those evolving techniques which will provide improvements in depth resolution, bulk detection limits or may lead to improved microanalytical and submicron lateral resolution capabilities.

The following provides a brief summary of these evolving techniques followed by a short comment as to their relative advantages and disadvantages. This will then be followed by a discussion of the relative analytical merit and a perspective on these techniques, as well as what might be expected if research is pursued in bringing these evolving techniques to bear on current or future materials or device technologies.

DESCRIPTION OF TECHNIQUES

I. Time-of-Flight SIMS

The first method that one can envision for improved detection sensitivity would combine the ability to detect most or all of the different elements contained in a given sample volume, coupled with the maturity and analytical sensitivity of SIMS. A conventional secondary ion mass spectrometer is a point focus, single ion detector. All other ions of potential analytical interest are lost. Thus, if one wishes to analyze ten different elements from a piece of material, one must consume ten unit volumes of that material. There are two approaches to simultaneous, multi-element detection. One is the use of an extended focal-plane mass spectrometer, and the other is time-of-flight mass spectrometry. At the present time there are no focal plane mass spectrometers in commercial production. They are expensive to construct and the necessary detector technology is quite immature. On the other hand, time-of-flight mass spectrometry is fairly mature. Commercial instruments are available for specific purposes, and the detector technology exists.

In TOF/SIMS, one would use a pulsed primary ion beam of oxygen or cesium ions, depending upon the desired secondary ion species coupled to a time-of-flight mass spectrometer for mass separation and detection. Although one would still achieve only the ion yields available with existing SIMS instrumentation, the value of this technique lies in being able to sample and collect all of the ions produced from a given pulse. Thus in the above example, if time-of-flight capabilities could be implemented, we would be able to detect all ten elements from a single unit volume of material, thereby increasing the effective sensitivity or detection limits of the SIMS technique by a factor of 10. The improvement would be even greater for survey analysis in any materials-limited situation such as the analysis of thin films or micro-areas. Such an enhancement of the multi-element detection capability of the SIMS technique will be necessary when performing survey analyses in submicron areas. The achievement of the submicron capability would be accomplished through the use of a microfocused ion source producing a high current density, pulsed ion beam. There exist high current density, liquid metal ion sources,

but they do not seem capable of long-term reliable operation, don't produce a beam of cesium ions and are difficult to pulse. Research in all of these areas is being pursued.

One of the main features of time-of-flight/secondary ion mass spectrometry is that it can be combined with techniques such as resonance or multiphoton ionization for enhancing the conversion of sputtered atoms to ions. Thus, the next generation TOF/SIMS instrument would combine the submicron analytical features of:

- 1) a liquid metal gun,
- 2) the ion yields of reactive ion bombardment SIMS or photo-enhanced ionization (resonance or multiphoton ionization),
- 3) the near 100% collection efficiency of a time-of-flight configuration, and
- 4) the simultaneous multi-element detection capability of the time-of-flight mass spectrometer.

There are two methods for enhancement of the atom-to-ion conversion process (discussed below), both of which could also be implemented on a time-of-flight SIMS instrument.

II. Resonance Ionization Mass Spectrometry (RIMS)

A variety of workers are currently investigating an evolving analytical technique which employs high power density laser irradiation to bring about the highly specific, highly efficient ionization of a desired atom sputtered into the vacuum. As implemented in present day configurations, the surface of the sample is sputtered using a pulsed ion beam followed by wavelength specific laser irradiation of the sputtered neutral plume so as to bring about a resonance ionization process leading to highly efficient, highly element specific ionization. This process can conceptually provide 100% conversion of atoms into ions and if combined with the proper mass spectrometer could provide near 100% collection efficiency of the ions thereby produced. Between concept and practice lies a host of problems: conceptual, physical and instrumental; which have prevented RIMS from fully achieving its capabilities. However, putting aside current problems, the RIMS technique holds the promise for being one of the most sensitive techniques for analysis of a specific element.

III. Multi-Photon Ionization Mass Spectrometry (MPIMS)

Multi-photon ionization mass spectrometry employs ion beam sputtering, pulsed laser enhanced ionization and mass spectrometry, as does resonance ionization mass spectrometry. However, in the MPIMS technique, one employs a sledge-hammer-like approach wherein photons of the highest possible energy or shortest wavelength are brought to bear on the cloud of atoms sputtered by a pulsed primary ion beam. If the photon density is sufficiently high in the sputtered neutral cloud and two or more photons arrive at the same time in the vicinity of a single atom, an electron is promoted from a ground state in that atom into the vacuum thereby producing a positive ion. In this manner, one can produce a broad elemental coverage by photo ionization rather than specific elemental excitation, as does resonance ionization. This technique can be employed for multielement excitation as does SIMS and is readily combined with a time-of-flight mass spectrometer. Interestingly enough, MPIMS should be as sensitive as resonance ionization for most elements with simultaneous excitation rather than being able to select a single element. The technique is quite new but already holds promise as a sensitive technique for the survey analysis of materials.

Comments on I, II, and III

It is interesting to note that the development of time-of-flight SIMS as originally proposed was to provide multielement detection to enhance the practical detection limits of submicron SIMS. At that time, we proposed the use of resonance ionization to improve detection limits for the analysis of a specific element. Now with the advent of MPIMS, it is possible that an additional mode of excitation could be brought to bear on microanalyses with an advanced TOF instrument.

The nature of time-of-flight SIMS demands the use of a pulsed ion production process so as to bring about the production of the ions in a very short time such that they are able to separate in time without a confusion of masses brought about by a long time of excitation. In the case of the two laser excited techniques, one must employ pulsed lasers to achieve the power densities necessary to bring about the desired saturation of the ionization process in order for these techniques to be truly competitive with conventional SIMS. Thus, in our letter of April, 1984, we requested a redirection of effort in order to bring forward the development of a time-of-flight/secondary ion mass spectrometer. We requested this, not only because of the unique capabilities offered by the TOF/SIMS instrumental configuration, but also because it provides a unique ion optical, analytical bench for next generation instrumentation. As originally proposed, the time-of-flight SIMS process is ideally suited to submicron ion probing for the survey analysis or multielement analysis of specific, localized areas.

Independent of the use of a finely focused probe or a broad area analytical ion probe, such a time-of-flight secondary ion mass spectrometer is concomitant to the concepts of resonance ionization or multiphoton ionization mass spectrometry. For this reason, we are convinced that by implementing this TOF/SIMS capability, we will be able to redirect the efforts of this contract so as to bring about the development of new instrumentation of central importance to materials characterization.

An important concept which evolves from the above discussions is that sputtering is a highly effective process for controllably removing atoms from a material and presenting them to an external method for excitation or ionization prior to mass spectrometry. Control of the position, size and rate of removal of the sputtered area provides the lateral and in-depth resolution required for a particular analysis. The ionization process accompanies the sputtering process in conventional SIMS. In the proposed TOF/SIMS configuration, control of ionization and sputtering is intertwined. For resonance and multiphoton ionization (as well as some of the techniques to be discussed below), the "sampling" and "excitation" processes can be separated and individually optimized to the needs of a particular analytical situation.

This theme of ion beam sputtering to sample the material of interest followed by subsequent ionization processes for improvement of the signal-to-noise ratio will be discussed with the following techniques. In the first technique the focus is on reducing the spectral interference background to improve signal-to-noise, while in the other two, emphasis is placed on increasing the signal.

IV. Accelerator Based Secondary Ion Mass Spectrometry (AB/SIMS)

As is widely known and discussed, the spectral interference due to molecular ions is the most severe problem limiting the intrinsic sensitivity of secondary ion mass spectrometry today. RIMS and MPIMS concepts are attempts to accomplish a reduction in the background produced by molecular ions and/or increase the analytical ion intensity, in order to achieve an improved signal-to-background ratio and hence improved detection limits for techniques employing sputtering. Based on an examination of the mechanisms of secondary ion or sputtered ion production, we believe that there is little that can be done to improve the efficiency of the ionization which occurs during the sputtering process. However, we feel that near-term efforts can be made to achieve a reduction in the spectral background encountered in conventional SIMS. Thus, we proposed and are studying the possibility of reducing the incidence of molecular ions and consequent spectral background through the use of laser oriented processes or MeV accelerator based secondary ion mass spectrometry. Accelerator based SIMS involves accelerating negative atomic

and molecular ions to MeV energies and directing them through a "semi-dense" material or gas which dissociates molecular species and positively ionizes all of the atomic and collisionally dissociated molecular species. Thus, accelerator based SIMS as well as laser based dissociation techniques can be regarded as techniques which invoke sputtering and ionization followed by some secondary, albeit non-ionization, process. In this case the secondary process is not to improve ionization efficiency but to reduce the background, given the atomic and molecular ionization processes which accompany sputtering. At the present time, we believe that the ionization processes involved in commercial SIMS instrumentation offers the best sensitivity for much of the periodic table. Only a few elements suffer due to a lack of ionization efficiency, while most limitations can be attributed to spectral interferences. Thus, this emphasis on the reduction of spectral interferences could bring the most benefit in the shortest time.

V. Sputtered Neutral Mass Spectrometry (SNMS)

If we are to pursue the concepts of ionization subsequent to the sputtering process, there are two mechanisms that we can examine, both of which employ the use of plasmas rather than laser based photo ionization as is the case with resonance and multiphoton ionization. The best understood of these non-laser processes is referred to as sputtered neutral mass spectrometry (SNMS) developed by Professor Oechsner at the University of Kaiserslautern, West Germany. Although Professor Oechsner has devoted most of his time to understanding the fundamental plasma processes involved, we feel the technique of sputtered neutral mass spectrometry provides the potential base for an excellent method to characterize materials important in semiconductor technology. In the SNMS technique, one employs ion bombardment in order to sputter-eject atoms from the material of interest into the vacuum. Thus, one obtains a flux of neutral atoms directed into a plasma chamber consisting of a cyclotron plasma operating on a low pressure of argon. The nature of the plasma is such that approximately 1% of the neutral atoms which enter the plasma become positively ionized by electron impact but do not undergo any hard sphere collisions with the low pressure argon atoms or ions. The ions produced in this cyclotron plasma are then directed into a mass spectrometer for detection. Given that this technique is implemented in the large area depth profiling mode, we can achieve certain very unique analytical capabilities. First, the bombarding ion beam can be of very low energy thereby providing good depth resolution. In fact, with proper electrode configurations, the ions from the plasma itself can be directed against the sample surface with energies in the 200 - 500 electron volt regime, thereby providing the optimum in depth resolution. Once the atoms are ejected from the sample surface either by a true ion beam or by the plasma ions, they enter into the plasma for ionization where the "matrix" is the plasma. Thus, we can

achieve a reduction in the matrix effect which plagues many analytical techniques. Any process which removes the atom of interest from the matrix before bringing about the analytical excitation can only provide improved quantitative capabilities. Thus, the use of a two step process, available with resonance ionization and multiphoton ionization can also be implemented with sputtered neutral mass spectrometry. The first, sputtering, provides the sampling of the material of interest, while the secondary process, photon bombardment or in this case plasma excitation, provides the generation of the analytical signal in a matrixless environment. Thus, sputtered neutral mass spectrometry appears to provide a quantitative capability heretofore unrealized with any of the other microanalytical techniques. Conceptually, resonance ionization and multiphoton ionization should be quite quantitative, but the only supporting data available is on sputtered neutral mass spectrometry. Based on these conceptual evaluations, CHARLES EVANS AND ASSOCIATES has independently prepared a proposal to DARPA under the auspices of the Small Business and Innovative Research Program in order to evaluate and develop sputtered neutral mass spectrometry for quantitative microanalysis. The following information, developed in conjunction with that proposal preparation, is provided for completeness in this Annual Report.

Throughout our studies of evolving techniques, it has become very obvious to us that the separation of sampling of the material and excitation of the atoms of interest can provide unique capabilities heretofore unavailable. Thus, we feel that sputtered neutral mass spectrometry provides several unique capabilities. First, the use of low energy ion bombardment provides the potential for depth resolutions which are not generally achieved with present profiling techniques. Secondly, the removal of the atom from the matrix prior to excitation provides a matrixless and, hence, highly quantitative capability that has yet to be achieved in any surface or microanalytical technique. Thirdly, the SNMS technique is quite amenable to the use of a finely focused ion beam probe, either DC or pulsed for sampling and the use of an extended focal plane or time-of-flight mass spectrometer for simultaneous detection.

It should be noted that taken in total, the efficiencies of:

1. sputtered atom introduction into the plasma,
2. ionization by the plasma, and
3. collection of the ions exiting the plasma chamber

are sufficiently low that SNMS cannot achieve the detection limits of conventional SIMS, much less be applicable to highly sensitive, submicron

analyses.

VI. Glow Discharge Mass Spectrometry (GDMS)

There is presently a new technique for bulk analysis which also employs sputtering for removing atoms followed by secondary excitation in a plasma, glow discharge mass spectrometry (GDMS). During the preparation of our proposal we did not consider this technique since it is truly a bulk analytical technique. However, due to our investigations during the first year of this research activity and the perceived need for improved bulk analytical technique, we propose that the glow discharge mass spectrometer deserves serious consideration as an advanced materials analysis technique. Over the past several years, a few investigators have employed glow discharges for excitation of impurities contained in a material. Basically, one places the sample in a DC plasma containing argon ions which sputter the surface of that material into the gas phase. In the DC glow discharge, electron impact and Penning ionization produces ions of the sputtered neutrals. The ions produced by the glow discharge are then introduced into a mass spectrometer for mass separation and detection. This technique has the potential for providing part per billion (ppb) detection limits in a bulk analytical mode. One obtains a pseudo-depth profile since the material is sampled via the sputtering process which erodes successively deeper layers of the material prior to ionization in the plasma. This technique appears to provide state of the art bulk analysis, much as spark source mass spectrometry did 20 years ago, but instead of using photographic plates with their extended processing times, one can use quantitative pulse counting with 10-20 minutes required to analyze up to 20 different elements in a given sample. We are presently giving serious consideration to and are presently evaluating GDMS for bulk analysis. Given the nature of the analytical process wherein sampling is provided by sputtering and ionization provided in a separate step we feel GDMS could be eventually molded into a technique to provide large area depth profiling with excellent sensitivities and depth resolutions.

COMPARISON OF EVOLVING ANALYTICAL TECHNIQUES

With this host of new analytical techniques, none of which have any tried and true capability as do the existing techniques of SIMS, Auger electron spectrometry and Rutherford Backscattering spectrometry, how does one determine the best place to put one's efforts? We offer the following as a perspective on the evolving techniques discussed above.

1. Secondary Ion Mass Spectrometry (SIMS) (We are including this technique as the existing, mature, analytical approach),
2. Time-of-Flight SIMS,
3. Accelerator Based SIMS,
4. Resonance Ionization Mass Spectrometry,
5. Multiphoton Ionization Mass Spectrometry,
6. Sputtered Neutral Mass Spectrometry, and
7. Glow Discharge Mass Spectrometry.

The topics to be discussed for this intercomparison will be:

- I. the mechanism of the ionization process at our level of understanding and how the mechanism relates to the ability of the technique to quantitated,
- II. quantitation,
- III. uniformity of ionization,
- IV. spectral features and spectral interferences,
- V. sensitivity of the technique which will be discussed as
 - a. the ionization efficiency or ion yield,
 - b. the volume sampled during the analysis, and
 - c. the extraction and transmission efficiencies of the ion source/mass spectrometer combination.
- VI. the lateral resolution capabilities,

VII. depth profiling capabilities, in particular the depth resolution that should be attainable, and

VIII. outermost monolayer or surface sensitivity.

The first thing to note about all of these techniques is that they are all using mass spectrometric analysis and detection. That is to say:

1. the techniques are all capable of providing full periodic table coverage from H to U, and beyond,
2. they all provide isotopic detection capability, and
3. they are not plagued by either detector noise or broad spectral backgrounds as one has with optical techniques. It is interesting to note that although resonance ionization is practiced using mass

spectrometry, it need not have a mass spectrometer since one should be able to provide the necessary elemental specificity by choosing the appropriate laser wavelength and detecting the ions of only the one element that are produced. However, given the level of maturity of the technique, it is incumbent upon a responsible user to employ a mass spectrometer as a detector to insure that there are not broad band secondary ionization processes taking place which would provide ions of molecular species or another element which would give erroneous results.

4. they are operated in a regime where single ion counting can be employed.

I. Mechanisms of Ionization. There is a basic difference between SIMS, time-of-flight SIMS and accelerator based SIMS, and the other evolving techniques. In the SIMS techniques, the ionization process accompanies the sputtering event; therefore, we do not have the opportunity to independently control the ionization process beyond the use of reactive ion bombardment with O or Cs ions for optimized ionization. At this time, the exact nature of the ion production process, either positive or negative ionization, is not well understood. The nature of the ionization process and its exponential dependence on the ionization potential or electron affinity provides very large variation in the ion yields. For elements with low ionization potentials (K, Na, Li) or a favorable electron affinity (Se and Te) we have very high ion yields approaching a 10 - 50% efficiency of conversion of sputtered atoms into secondary ions. Alternatively, for those species with very high ionization potentials and unfavorable electron affinities (Zn, Cd and Hg being the classic examples), we have some four or five orders of magnitude lower ionization efficiency. Needless to say, the lack of

understanding of the ionization process and the broad variation in ion yields leads to difficulties in quantitation and large variation in the relative sensitivities of elements that might be analyzed.

Of the remaining techniques of resonance ionization, multiphoton ionization, sputtered neutral mass spectrometry and glow discharge mass spectrometry, all employ ionization mechanisms which occur after the sputtering event and can be considered to occur separated in time as well as in space. As discussed above, both resonance ionization and multiphoton ionization employ laser irradiation to bring about a post sputtering photo ionization process. In resonance ionization one must bring in at least one if not two laser beams of a specific wavelength to bring about the selectivity fundamental to resonance ionization. Thus, at least theoretically, ionization of a single element or even a single isotope can be accomplished, and all the other sputtered species are not ionized and thus do not complicate the analysis. In multiphoton ionization one uses a brute force method employing very short photon wavelength, (250 nanometers or less), to bring about non-specific multiphoton absorption by all the sputtered atoms. The power density is such that two or more photons arrive in the same position in space and time, in order to bring about the ionization. In the case of resonance ionization, there is essentially 100% ionization of the atoms of interest present in the volume defined by the laser beam and the sputtered neutral atom plume. Atoms present outside that volume are not ionized. In the case of multiphoton ionization there is a 100% ionization of most of the atoms present in that volume defined by the laser and the sputtered neutral plume. However, if an atom with a sufficiently high ionization potential is present, there may be an insufficient number of photons to provide enough energy to bring about a 100% ionization. For example, if we employ 3eV photons and must examine an element with an ionization potential of 10eV, then at least 4 photons must be present within a very short time at each atom; if not, then there will be no ionization. Of the other two techniques involving auxiliary or post-ionization, SNMS and GDMS, both employ a plasma or plasmalike process to bring about the ionization. For sputtered neutral mass spectrometry, the sputtered atoms are introduced into a low energy, low pressure plasma where approximately 1% of the atoms that enter the plasma are ionized by electron impact mechanisms. There is a small but measurable variation in the ionization efficiency (a factor of 10) across the periodic table. Although this sounds quite large, remember that with SIMS there is a $10^3 - 10^5$ variation in sensitivity or ionization efficiency. Moreover, the variation in SNMS ion yield from element to element is constant, and the ion yield for a given element is constant or reproducible. Thus, the number of ions produced per atom of a given element traversing the plasma is always constant, i.e. the conversion or relative sensitivity factor for a given element is independent of the matrix from whence it came. Thus, a standard of boron in silicon could

be used to quantitate the analyses of boron in GaAs, steel, etc. Glow discharge mass spectrometry is similar to SNMS, in that the sputtered atoms are introduced into a plasma, a glow discharge in this case, wherein there is ionization by electron impact as well as Penning ionization. Although the exact nature of the ionization is not well understood as well as in the other post ionization techniques, the ionization efficiency is good and most importantly the uniformity of the ionization from element to element is excellent. The most important aspect of these four auxiliary ionization techniques is that the ionization takes place external to the sample or matrix and in a region of somewhat uniform composition. In the photo ionization techniques the vacuum acts as the matrix, while with sputtered neutral mass spectrometry and glow discharge mass spectrometry, the argon based plasma is the matrix.

II. Quantitation. In order to quantitate a mass spectrometric technique (as with any analytical technique), one must convert the measured ion intensity from counts per second or amperes per second into concentration. With almost any analytical technique, one employs either:

1. standards wherein the conversion factor is calculated from samples containing known concentrations and measured ion intensities or,
2. an empirical method for calculating the sensitivity factor based on first principles. For a variety of reasons we propose that one must employ standards. In the case of these techniques, all employing sputtering, we must know several factors in order to quantitate:
 - a. the number of atoms sputtered from the sample per unit time,
 - b. the conversion efficiency of atoms into ions or the ion yield,
 - c. the number of ions extracted from the ionization volume into the mass spectrometer (the extraction efficiency),
 - d. the transmission efficiency of the mass spectrometer, and
 - e. the detection efficiency or quantum efficiency at the detector.

Determining these from first principles and keeping them constant over a long period of time would be difficult, if not impossible. Thus, in all cases, we must use some sort of standardization process. It is important to remember that the ion yields can vary not only from element to element but from one material to another, i.e. the matrix effects. Matrix effects are processes taking place during ionization which lead either to a nonlinear relationship between ion intensity and concentration or change the ion intensity produced for a given element when changing from one matrix to another. That is to say, B in Si may well have a different ion yield than B in GaAs. In light of these concepts, let us now examine the quantitative aspects of the evolving

techniques. As is implied by the previous discussion secondary ion mass spectrometry (conventional, TOF and accelerator-based) requires the use of standards in order to accurately convert ion intensity into concentration. Since the ionization efficiency varies by large amounts from element to element, one can not merely ratio the intensity of two elements in order to obtain a concentration ratio. Moreover, since the ionization takes place in or near the surface of the sample (matrix), SIMS is susceptible to matrix effects which can produce a different ion yield for given element from one matrix to another. Thus standardization is imperative. Given that one has standards which very accurately mimic the unknown in composition at the matrix level, then quantitation can be good to excellent. For instance, if a given B implant is analyzed 5 or 10 times, standard deviations of better than 5% can be obtained. The same is true at major constituent levels, as we have shown in the above discussion of BPSG quantitation using externally generated standards. The real difficulties in quantitating SIMS come in trying to determine the relative concentrations of two elements in the same material for which there are no standards or for quantitating impurities in a matrix for which no standards are available.

Although the variation in ionization efficiency is not as great for the four post ionization techniques as it is for SIMS, many of the same basic considerations are required for quantitation. That is to say, how do I convert the number of ions detected into a concentration in the matrix of interest? Of course, the techniques of resonance ionization, multiphoton ionization, sputtered neutral mass spectrometry and glow discharge mass spectrometry are all amenable to quantitation using standards. However, if the mechanisms of ionization are as proposed and one is able to control the sputtering process or at least understand the sputtering process, one should be able to go beyond the requirement for standards and begin to perform semiquantitative analysis without a standard. Certainly this is possible by multiphoton ionization, sputtered neutral mass spectrometry, glow discharge mass spectrometry and probably multiphoton ionization as shown by the workers in these three areas. In these cases, one is bringing about the ionization of all of the species sputtered from the sample, either with the laser as in MPIMS or by the plasma in SNMS and GDMS. Since these techniques show a fairly uniform excitation across the periodic table (i.e., across ionization potentials), then one should only need to take the intensity of any element, divide it by the sum of the intensity of all the elements to obtain a semiquantitative analysis. In a material with a single major constituent one merely takes the intensity of an impurity, divides it by the intensity of the matrix ion (after correction for isotopic abundances) to obtain a semiquantitative measure of the concentration of that species in that matrix.

The phenomenon central to this semiquantitative approach is the external or

post sputtering ionization processes involved in these techniques. For example, the success of this approach has been shown by the one group using glow discharge mass spectrometry. In the case of a copper matrix, they found no more than about a 15% change in ionization efficiency or sensitivity across an approximately three electron volt variation in ionization potential. As was said earlier, the sputtered neutral mass spectrometry technique has demonstrated uniform ionization to within a factor of 3 to 10. With the multiphoton ionization technique so immature, we can only draw a conceptual conclusion.

Resonance ionization, on the other hand, is in a way caught between the difficulties of SIMS and the theoretical ability to quantitate from first principles. If one assumes that all of the parameters influencing the introduction of neutral species into the ionizing volume (the sputtering process) and the if extraction and transmission efficiency of the mass spectrometer stay constant, then one could assume 100% ionization for any element under study and arrive at a concentration. Unfortunately, there are nuances of the resonance ionization process that are rarely taken into consideration:

1. The sputtering rate of a given material controls the rate of ejection of the neutral atom of choice which yields the detected ion intensity. Thus, without a knowledge of the rate or volume of matrix removal, how is the assumption of 100% ionization converted into a concentration?
2. The solid angle of emission and hence the number of neutral atoms subtended by the laser beam can vary due to crystallographic effects and from material to material.

The specificity of the resonance ionization process may be so great as to excite only those atoms present as ground state neutrals and ignore those atoms emitted as excited neutrals, positive or negative ions or as molecular species. Thus the excitable atom pool is dependent on the secondary ions formed and the variation in molecular species formed. Some of the problems could be mitigated by monitoring the intensity of a matrix ion. However, the technique of ionization is so specific, a two ionization process (one laser-photon process exciting the impurity of interest and the other exciting the matrix of interest) would be necessary. This would seem to be quite expensive.

III. Uniformity of Ionization. Having discussed the mechanism of ionization and quantitation, we have basically addressed the uniformity issue. Given data that exists to date, we would say that glow discharge mass spectrometry has the most uniform ionization followed by sputtered neutral mass

spectrometry. We have seen no data which speaks to the uniformity of ionization of different impurities and different matrices for multiphoton and resonance ionization. From first principles, we would argue that they are next in line from a uniformity standpoint, followed by conventional and TOF SIMS, and accelerator based SIMS would be the worst.

IV. Spectral Features and Spectral Interferences. As with any analytical technique employing spectroscopy, be it optical or mass, we must be concerned about the nature of the spectrum and the backgrounds present, and the consequent impact on signal to background, sensitivity, and attainable detection limits. Mass spectrometry rarely has any continuum spectral features as are commonly encountered in optical spectroscopy. Mass spectrometry can have one of three kinds of spectral interferences:

1. Isobars are isotopes of two different elements having masses sufficiently close together as to be inseparable within conventional resolution.
2. Multiply charged ions are species for which the charge-to-mass ratio cause them to be detected at one-half of their actual mass, where there may be an ion of interest.
3. Lastly, molecular ions are species which result from the association of two or more isotopes which then may fall at a mass of interest.

Thus, any mass spectrometric technique must deal with these spectral features which can result in an undesired signal occurring at the mass of interest. Generally speaking, any technique which is used to reduce the incidence of an interfering species will require the reduction in another analytical feature. Traditionally, the reduction of a spectral interference is obtained by the use of high mass resolution techniques wherein one can resolve the exact mass differences which generally occur between any two ions. The hardest interferences to resolve are isobars since the exact masses may vary by as small as one part in 10^5 or 10^6 . Multiply charged ions are either very difficult to resolve since they act much as isobars or are no problem at all since the doubly charged ions of an odd isotope would occur at a half mass, far away from the mass of interest. In the case of molecular ions, we reach an intermediate resolution requirement wherein mass resolutions of 500 to 10,000 are required to reduce the effect of the molecular species. Secondary ion mass spectrometry produces few multiply charged ions, is rarely plagued by isobars but does encounter a large number of molecular ions. The variety of techniques which are used to reduce these spectral interferences include Voltage Offset and High Mass Resolution (please see the attached application notes which have been generated some years ago by CHARLES EVANS AND ASSOCIATES explaining these two modes of operation.)

Time-of-flight SIMS will, of course, be plagued by the same spectral problems as conventional SIMS but would not have the opportunity to use high mass resolution due to the spectral resolutions obtained in a time-of-flight mass spectrometer. Of course, accelerator based SIMS is founded on reducing the incidence of spectral interferences at low mass resolution and is quite successful. One discriminates against isobars since each of the isobaric species will have a different atomic number or Z and, therefore, will be stripped of its electrons to differing extents in the stripping process and will have a different response in the Z sensitive detectors used by AB/SIMS. These detectors allow discrimination between two elements at the same mass but which have different atomic numbers. Multiply-charged ions are not produced during the negative ion production required of AB/SIMS, and the incidence of variable charged states at the detector end are easily taken care of by the charge and mass spectroscopies used in this technique.

In theory, resonance ionization provides such elemental selectivity in the ionization process that one can select the exact element of choice such that isobaric interferences, doubly charged ions or molecular ions will not be produced. To date there have been reported several instances of broad band excitation or alternate pathways which do lead to the production of undesired ions. However, the incidence of a spectral interference is still very, very small, and this technique probably represents one of the most successful techniques at reducing spectral interferences (accelerator based SIMS being second most successful). Multiphoton ionization is in a state of infancy, and, although we cannot comment specifically on the processes, multiphoton ionization may well lead to partial reduction of spectral interferences by dissociation of some of the undesired molecular ions. We do know that the second ionization potentials are high, thus there is a low probability of doubly charged ion formation, and the technique will have to deal with isobaric interferences, although their incidence is low in most materials. Both the sputtered neutral mass spectrometry and glow discharge mass spectrometry employ a sufficiently low energy of ionization that multiply charged ions are rarely encountered and isobarics must be dealt with as with any mass spectrometry technique. Again, due to the infancy of the techniques, conclusions on the impact of molecular ions are difficult. In sputtered neutral mass spectrometry singly charged molecular ions are observed, but their incidence seems to be quite low. In glow discharge mass spectrometry, the pressure in the plasma is quite high, and we feel that there is a sufficient amount of dissociation of molecular species that the incidence of molecular ions is very low. Based on the limited amount of data, glow discharge mass spectrometry would seem to show a low incidence of spectral interferences because the ionization is fairly gentle, producing very low kinetic energy ions, hence, there is ample opportunity for using high mass

resolution. To date, the technique has shown the ability to operate with sub part per million detection limits while operating in the high mass resolution mode in the presence of severe multiply charged and molecular ion interferences.

V. Ultimate Sensitivity. Sensitivity can be defined in several ways. Sensitivity can be the overall efficiency of the measurement process, i.e. the number of ions detected per atom in the sample, or it can be the absolute detection limits in ppm or ppb. The ultimate sensitivity of the techniques can be influenced by several features which can only be partially deconvoluted. The ultimate sensitivity of any of these techniques is the product of many factors. If we think in terms of detection limits being determined by the intensity of the element of interest (in the absence of a spectral interference, then):

$$\frac{\text{ions detected}}{\text{sec}} \cdot \frac{\text{atoms sputtered}}{\text{sec}} \cdot \frac{\text{ions produced}}{\text{atom sputtered}} \cdot \frac{\text{ions collected}}{\text{ion produced}} \cdot \frac{\text{ions transmitted}}{\text{ion collected}} \cdot \frac{\text{ions detected}}{\text{ion transmitted}}$$

Although all of these factors can strongly influence the attainable detection limits, there are two which most significantly differentiate the techniques under discussion:

1. the numbers of atoms sputtered per second since this parameter affects the number of atoms available for signal generation, and
2. the number of ions produced per atom sputtered since this step is potentially the most limiting step in the generation of analytical signal from the sputtered atoms.

To a lesser degree, the collection efficiency of the mass spectrometer optics is also highly controlling. The nature of the ionization process, and the angular and energy divergence of the ionization process, the angular and energy acceptance of the mass spectrometer are central in the matching of the emission characteristics of the ion source and the efficiency of acceptance by the mass spectrometer. The following discussion will comment on those aspects of each technique which are critical.

The number of atoms sputtered per second represents the results of a variety of physical and instrumental parameters such as the area sputtered (microanalytical versus macro- or bulk analytical) and the linear rate of removal (Angstroms/sec). In the case of the pulsed sputtering techniques (TOF/SIMS, RIMS and MPIMS) the linear rate of removal can be quite low due to short "on" time (10-100ns) and the low repetition rate (10^3 for TOF/SIMS and

10-30 per second for RIMS and MPIMS). On the other hand, the sputtering rate and the area sputtered can be very large for the bulk or large area profiling techniques of AB/SIMS, SNMS and GDMS.

The ionization efficiency is the ability to convert a sputtered atom into an ion and is one of the most critical issues in determining the overall sensitivity of a technique. In conventional SIMS the combination of reactive ion bombardment and the analysis of species with moderate to low ionization potentials (less than or equal to 9eV) or moderate to high electron affinities (greater than or equal to 1eV), the secondary ion yield can be of the order of 1-50%. When operated at low mass resolution, the collection and transmission efficiency of an optimized secondary ion mass spectrometer (i.e., the Cameca IMS-3f) can be 10-50% depending on the exact operating conditions. Thus, for a significant number of the elements in the periodic table, one ion per hundred to one ion per thousand atoms sputtered can be detected. For time-of-flight SIMS we can expect the same ion yields and perhaps even higher extraction efficiency. Additionally, TOF/SIMS offers the efficiency of SIMS coupled with the ability to detect all masses sputtered from a given volume of material, thereby improving the effective detection limits by at least a factor of ten.

Both resonance ionization and multiphoton ionization mass spectrometry tend to have very high ionization efficiencies for the atoms sputtered from the sample which are in the volume defined by the laser beam and the sputtered neutral plume. Any species falling outside this region are not ionized. For RIMS the ionized ratio is said to be 5-10%, and an estimate for multiphoton ionization would be 1-10%. Moreover, for both of these techniques (and for TOF/SIMS, to a lesser degree), the volume of material sputtered per unit time is exceedingly small due to the low duty cycle of the pulsed ion source and the pulsed lasers. The collection and transmission efficiencies can vary depending on the mass spectrometer design. Resonance ionization is much like conventional SIMS and AB/SIMS, in that the mass spectrometers presently in use detect only one mass at any given instant, therefore, losing the data produced at all other masses. Multiphoton ionization is at present implemented on a time-of-flight system, combining the high ionization efficiencies of the multiphoton ionization process with the high transmission and simultaneous or multielement detection of the time-of-flight mass spectrometer. From the previous discussion, it becomes clear that one could practice RIMS or MPIMS on a TOF/SIMS with the addition of some timing electronics and the appropriate laser or lasers. Hence, our proposal to begin the design, assembly and testing of a TOF/SIMS.

The necessary use of a tandem accelerator for accelerator based SIMS requires the use of Cs ion bombardment and negative ion spectroscopy SIMS. This is

fine for those electronegative species that form negative ions with a high efficiency. In the case of the electropositive elements for which one conventionally employs oxygen ion bombardment, techniques have been developed for enhancing the production of negative ions containing the element of interest. Generally this is accomplished by flooding the Cs bombarded surface with oxygen to produce molecular species with a high electron affinity which are then dissociated in the stripper step in order to provide the atomic ion of interest. The mass spectrometers employed for accelerator based SIMS are low resolution, high ion transmission systems, thus we have fairly good ion collection and transmission through the system. The detectors are based on pulse counting techniques and therefore give very high detection sensitivities. Thus, the sensitivity of accelerator-based SIMS is quite good, and it has yet to be fully assessed as to its true quantitative ability.

Sputtered neutral mass spectrometry provides ionization efficiency of about 1% of the atoms sputtered from the sample which traverse the ionizing plasma. The proportion of atoms introduced into the plasma in this technique has yet to be assessed. Depending upon the mass resolutions required, sputtered neutral mass spectrometry should be capable of transmissions approaching that of a conventional SIMS under the same mass resolution conditions. Thus, the technique is almost certainly capable of sub-ppm detection limits. Glow discharge mass spectrometry consumes material at a very high rate since sputtering occurs on a broad front, thereby providing a very high rate of introduction of species into the ionizing volume, but the high ionization efficiency on the ionizing plasma has yet to be assessed. The coupling of reasonable extraction efficiency and high transmission mass spectrometry leads to very good detection limits for this technique. The technique has already exhibited bulk analysis sensitivities on the order of 1-10 parts per billion, and the technique is only evolving. At the present, the GDMS technique seems most suited to trace element bulk analysis.

VI. Lateral Resolution. The next analytical feature to be discussed is that of lateral resolution, which governs the ability to obtain an analysis of a specific localized area or to provide an ion image depicting maps or pictures representative of the relative distribution of a given isotope or element. There are two instrumental ways to achieve ion images. One is through microprobing techniques, wherein a microfocused source of excitation is brought to bear on the region of analytical interest. An ion image is generated by rastering that excitation about the sample surface so as to sequentially sputter microscopic areas on the sample and then use the mass spectrometer output to modulate the intensity axis of an oscilloscope which is synchronously rastered with this exciting beam. The alternative approach is to use ion microscope techniques wherein specialized ion optics are used to extract an ion image of the sputtered ions while maintaining the relative

position of the ions as they are emitted from the surface. Thus, in a ion microprobe, one generates the picture points or pixels of the ion image sequentially much as a TV screen generates an image sequentially. Alternatively, the ion microscope generates picture elements from all areas on the surface of the sample simultaneously much as an optical microscope provides a light image of the surface of the material. For a variety of reasons which are beyond the scope of this report, the ion microscope technique is the best way to provide ion imaging, and it also provides the best "all around" depth profiling capabilities. However, it does suffer from the difficulties in localizing the analysis to a small portion of a sample, as can easily be done with microprobe techniques.

Conventional secondary ion mass spectrometry can be practiced either in an ion microprobe or ion microscope mode of analysis. Commercial instruments are available for both modes of operation, but the most developed technology and most broadly used instrument happens to be an ion microscope (the CAMECA Ion Microanalyzer). The lateral resolution capabilities of the ion microprobe and ion microscope can be easily considered microanalytical. Ion microscope instrumentation, as presently conceived, provides lateral resolutions of the order of 0.3 to 0.5 microns on well behaved samples. At the present time, commercial ion microprobes are capable of lateral resolutions using a beam focused to the order of 2-5 micrometers. Thus the present ion microscope instrumentation provides much better lateral resolution. At the present time, one can envision improvements on the incremental front to the lateral resolution to the ion microscope, bringing its resolutions to the order of 0.1 to 0.25 micrometer. Lateral resolutions with the ion microprobe can be dramatically improved through the use of high intensity liquid metal ion sources. These liquid metal ion sources should provide lateral resolutions of the order of 0.1 to 0.2 micrometer if implemented on conventional SIMS instrumentation. As was discussed in the proposal which resulted in this contract, the number of atoms available for an analysis is governed by the area of the analysis, all other things being equal. Thus, if we were to implement microanalysis at the submicrometer level, a host of other instrumental advances will have to be accomplished in order to maintain the desired sensitivities. If this is to be done with ion microscope instrumentation, we will have to develop the ability to laterally discern or depict the area of ion emission quantitatively. Such is the idea for the use of digital imaging processing, which we are implementing under another contract. An alternative approach is the use of the liquid metal ion source for an ion microprobe based analysis. If submicrometer capabilities are to be obtained with the ion microprobe, reliable, long term metal ion sources must be developed. This process is being pursued by several government and privately funded research efforts. One of these efforts is our subcontract under the auspices of this grant to the Oregon Graduate Center for development

of a liquid metal ion source.

We feel that the second most important consideration for achieving a viable analysis from submicron lateral resolution capabilities is the implementation of parallel ion detection of all the ions produced during a given sputtering event so as to efficiently utilize the data that is made available during a microanalysis. This is the basis for our recommendation and proposal to develop a time-of-flight spectrometer in anticipation of attaining submicron lateral resolutions with good elemental coverage. We should note that parallel ion detection can be achieved with a focal plane mass spectrometer, however, such instrumentation is not commercially available and would be very expensive to design and implement and is not within the budgetary scope of this contract. Moreover, time-of-flight SIMS is easily combinable with the pulsed laser requirements of multiphoton ionization, as well as resonance ionization techniques.

As implied by the previous discussion, submicron lateral resolution could be attained with either resonance ionization or multiphoton ionization using ion microprobe concepts, if we can overcome the problems associated with pulsing the submicrometer ion beam. At this time we would be hesitant to say whether one could use ion microscope techniques with these post ionization concepts (RIMS, MPIMS and SNMS) since the energy and angular divergence of the ion beam will be exaggerated by the post ionization process and may lead to problems in stigmatically focussing these ion sources. Lateral resolution capabilities of accelerator based SIMS are presently nonexistent; that is to say, all the instruments in existence use a 1 mm or larger primary ion beam. However, there is nothing fundamental to prevent the implementation of microfocused ion beams, just as could be done for SIMS, TOF/SIMS, RIMS, MPIMS or SNMS. However, the collisional processes involved in the AB/SIMS stripping process would probably preclude ion microscope methods. Sputtered neutral mass spectrometry, as mentioned above, would be like any of the post ionization techniques (RIMS and MPIMS) in which a liquid metal ion microprobe could be easily employed, but SNMS would probably not be amenable to ion microscope techniques. Given the nature of the glow discharge process, wherein a large area, high pressure plasma contacts and sputters the surface of the sample, we can presently see no possibility for microprobe or microscope imaging. It is possible that sputtered neutral mass spectrometry could be implemented on an ion microscope, but it would face the same difficulties as resonance or multiphoton ionization, i.e. the energy and angular dispersion of the ions and the potential for scrambling of the image prior to the ionization process.

VII. Depth Profiling. The last analytical feature to be discussed is that of the ability of the techniques to provide a depth profile and the potential depth resolutions attainable by each of the techniques. SIMS is already a

highly accomplished depth profiling technique providing depth resolutions of the order of a few tens to hundreds of Angstroms or 1% of the depth sputtered, in a well behaved sample. These depth resolutions are accomplished over analytical areas of the order of 150 micrometers in diameter and provide detection limits which range from 10^{13} - 10^{17} at/cm³, depending upon the ion of interest. Conceptually, there is no reason that accelerator-based SIMS, resonance ionization or multiphoton ionization could not provide depth profiles. At the present time the instrumentation does not. Accelerator based SIMS is still operating in the bulk analysis mode while the present day instrumentation for resonance ionization or multiphoton ionization leads to little or no capability for depth profiling over significant depths due to the low duty cycle for sputtering available from the instrumentation. Sputtered neutral mass spectrometry technique can and does perform depth profiles using either an external ion beam (as does SIMS, RIMS and MPIMS) or by bringing the plasma (also responsible for ionization) in contact with the sample surface in order to erode the surface in a highly controlled fashion. Since the argon ions from the plasma are initially at a low energy (10-20eV), their impact energy can be controlled to be of the order of 100-300eV. This is sufficient to bring about the sputtering process but allows for minimal ion beam mixing. At the present time sputtered neutral mass spectrometry probably has the best depth resolution of all of the profiling techniques.

Glow discharge mass spectrometry, as it is presently configured, does not provide for depth profiling in a controlled fashion. Although the sputtering process that is used to introduce the ions into the ionizing plasma sequentially sputters surface layer after surface layer, this is accomplished with no regard for geometry, thereby leading to poor depth resolution albeit a sequential layer removal process.

During this study we have isolated an important analytical requirement. The need to perform a highly sensitive surface analysis for an impurity or impurities of interest, or, more importantly, to provide a full periodic table coverage survey analysis while constraining the analysis to the outermost few monolayers or to a few monolayers about an internal interface. Conventional secondary ion mass spectrometry has the sensitivity to achieve this if one operates under low mass resolution conditions and does an element by element analysis. Inherently, accelerator-based SIMS should provide the same basic surface sensitivities as conventional SIMS, with the added benefit of reduced spectral interferences. Spectral interferences can be somewhat problematic in a surface analysis since there are a host of impurities and environmental contaminants present on the surface which lead to a prodigious number of molecular ions. Time-of-flight SIMS has the potential for providing an exceedingly sensitive survey analysis of the surface of the material. Since it is a pulsed technique, one can change the pulse repetition rate and duty

cycle in order to sputter as little or as much of the surface per unit time as might be desired. This controllable sample rate combined with the high ion yields inherent in SIMS and the high transmission capabilities of a time-of-flight SIMS make the parallel detection capabilities of the time-of-flight SIMS highly useful in any multielement or survey analysis.

Resonance ionization, if it lives up to the promise of being the most sensitive of the techniques, would be a very good surface analysis technique in that it is pulsed, and one can control the erosion rate. However, it is severely limited by the need to use a specific wavelength laser combination for each individual element. Thus, one would take hours or days to accomplish a single multielement survey analysis of the surface of the material which the other techniques could accomplish in 15 minutes. Multiphoton ionization, on the other hand, would have very close to the same sensitivities as resonance ionization; however, it would far exceed resonance ionization in the ability to analyze impurities on the surface due to the broad elemental coverage of the excitation and the use of time-of-flight mass spectrometry for parallel ion detection.

At this point we reach a variety of tradeoffs which requires that we consider the general requirements of a laboratory or a specific analysis. For example, TOF/SIMS and MPIMS have very good to excellent ionization efficiencies, provide parallel detection for multielement or survey analysis but would suffer from spectral interferences. On the other hand accelerator based SIMS and RIMS would have minimal spectral interferences and would have good to excellent ionization yields but would detect only one mass of the many produced at any given time.

VIII. Proposed Approach. We see the following as the direction we are corporately pursuing and the direction for DARPA consideration. Secondary ion mass spectrometry is a well known, very mature technique and has potentials that are as yet undeveloped. We hope to achieve these through the molecular dissociation aspects being pursued under this contract and to evaluate accelerator based SIMS as a component of these undeveloped capabilities of SIMS. At the present, glow discharge mass spectrometry seems to be well developed instrumentally but does need applications orientation. Although not within the proposed activities of this contract, we are sufficiently convinced of the viability of glow discharge mass spectrometry that we will probably add a system to our analytical capability by the end of 1984.

On the instrumentation development front, we would propose two parallel activities: one is the development of a time-of-flight SIMS instrument in order to hasten the available of this parallel detection technique combined with its capabilities as a workbench or ion optical bench for the development

of multiphoton and resonance ionization techniques. The second is the development and evaluation of sputtered neutral mass spectrometry as a next generation technique for quantitative microanalysis and depth profiling.

Obvious by its omission is an emphasis on resonance ionization concomitant with its reputed potential. At the present time there are four Federal laboratories, one university research group and one Federally funded, private laboratory pursuing RIMS. Until some of the potentials are recognized, the above support and activity seems sufficient.

IX. Commercial Availability. As implied by the previous discussion, only conventional SIMS is commercially available today. Glow discharge mass spectrometry will soon become available with the introduction of the VG 9000 sold by VG Isotopes of the United Kingdom. Although accelerator based SIMS is commercially available in concept, the implementation of the instrumentation is a somewhat laborious process and still requires some maturation before it can achieve routine, day-in-day-out utility. Neither time-of-flight SIMS, resonance ionization, multiphoton ionization nor sputtered neutral mass spectrometry are commercially available. The development of a time-of-flight SIMS under this contract could bring forth a commercial instrument, one to three years sooner than would otherwise occur. More importantly, not only would this bring forth a new capability to the materials characterization, materials research community, but the implementation of a time-of-flight SIMS would also hasten the commercial availability of multiphoton ionization and resonance ionization instrumentation.

X. Summary of Strengths and Weaknesses. If we examine each of these evolving techniques, with conventional SIMS as a benchmark, we see that each one has specific capabilities. First, SIMS, as commercially available, is a mature technique which can provide depth profiles and lateral resolutions concomitant with many of the requirements of the semiconductor materials community, has outstanding sensitivity for most elements of interest, and can provide good quantitation, if standards are available. Its most serious limitations are the need for standards in order to provide semiquantitative or quantitative analysis and the prevalence of spectral interferences from molecular ions. Accelerator based SIMS is a very immature technology for semiconductor analysis although several instruments exist in research laboratories around the world. (None are yet available in the United States.) This technique has the potential for being an extremely valuable technique for the bulk analysis of semiconductor materials. Its quantitative requirements are that of SIMS but that is less of a problem for bulk analysis. Although it has minimal lateral or depth profile capabilities at the present time, its overall potential for a rapid analysis of one or more elements in a material make it a highly viable technique for the bulk characterization of semiconductor

material. This potential is borne out by our proposed investigation of this technique.

Looking at the next most mature technique, we find glow discharge mass spectrometry was relatively unheard of a year ago due to its rather obscure beginning. At the present time, one vendor is offering a glow discharge mass spectrometer, the first instrument to be delivered some time later this year. The technique, although lacking lateral and depth profiling capabilities, will potentially come on line for the bulk analysis of semiconductor material within six to twelve months at a significant level of sophistication. In the short term, it will probably compete with accelerator based SIMS, since GDMS has the potential for excellent standardless quantitation. Even though GDMS should meet short term demands for the bulk analysis of semiconductor materials, just as SIMS has for the last five years, we will need some technique three to five years hence, to go below 1ppb or 5×10^{13} at/cm³. Accelerator based SIMS is presently seen as the technique most probable to meet this need.

The remainder of the techniques of time-of-flight SIMS, resonance ionization mass spectrometry, multiphoton ionization mass spectrometry and sputter neutral mass spectrometry are still immature techniques. We see their potentials for development as the following:

1. sputter neutral mass spectrometry shows great potential as a microanalytical technique with parts per million detection limits and excellent quantitation. The lateral and depth profiling capabilities should be as good as any of the other techniques, and its only shortcoming will be the potentially reduced sensitivities as compared to the other techniques due to its low overall ionization efficiencies. Thus, SNMS does not vie for the role as the most sensitive for bulk analysis nor does it promise to be the most sensitive in terms of overall efficiency of conversion of atoms into a collectable signal. However, it could become the next versatile technique providing lateral resolutions of the order of one micron, depth resolutions better than presently attainable, sensitivities of a part-per-million and a matrixless, standardless, quantitative capability. Thus, it has the potential for competing with Auger electron spectrometry, scanning Auger microscopy and even perhaps the electron microprobe as a technique of choice in the next five years. To our knowledge there is only one laboratory in the world working on sputtered neutral mass spectrometry, and that is in the laboratory of the developer, Professor Oechsner in West Germany.
2. At the present time, there is only one laboratory actively pursuing multiphoton ionization, Stanford Research Institute. The potential for

the technique has yet to be fully achieved, but it does seem that it will provide a moderate quantitative capability, with 0.1 to 1 part per million sensitivities with the ability for lateral and depth profiling analyses dependent upon enhancements to the instrumentation in the ensuing years.

3. Resonance ionization is being pursued in a few laboratories and is nowhere near commercial availability or viability. At the present time its real capabilities lie in its potential for very good detection limits and the absence of spectral interferences. Lateral and depth profiling resolution capabilities are well into the future, and it will hardly achieve the capabilities of being a rapid survey analytical technique. Its real features lie in the ability to provide exceedingly sensitive, highly selective analyses.
4. Time-of-flight SIMS is presently available in only one laboratory in the world, and it has the potential of being a very viable technique since it combines the ionization and quantitation features of an existing, highly developed technique, conventional SIMS, and the parallel detection capabilities of time-of-flight. Moreover, it should provide very good surface sensitivity and the instrumentation is an ideal foundation for implementing multiphoton ionization or resonance ionization.

FISCAL STATUS

- I. Incremental funding for the contract to date is \$330,000 for the period ending November 15, 1984
- II. Expenditures and commitments to date are:
 - a. \$157,507.57 as of 3/31/84
 - b. \$168,738.27 as of 4/25/84
- III. The present incremental funds will be required to perform the recently requested modification to the work statement.
- IV. As requested, a six month, no cost extension will be necessary to complete the efforts requested in the modification to the work statement.
- V. The direct labor costs have been averaging \$4600 per month over the last three months.

**SIMS P/Si Intensity Ratio vs.
Electron Microprobe P atomic %**

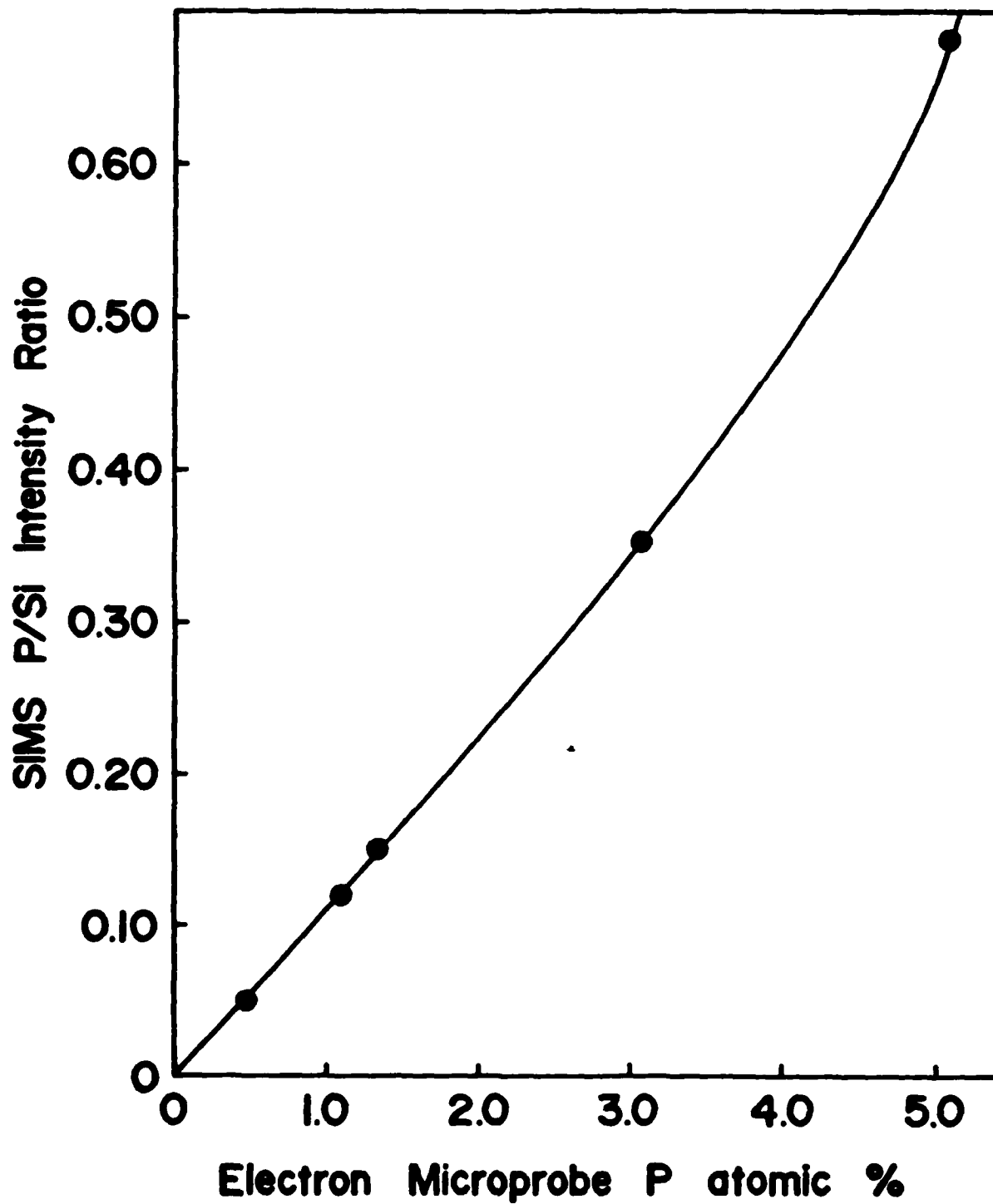


Figure 1

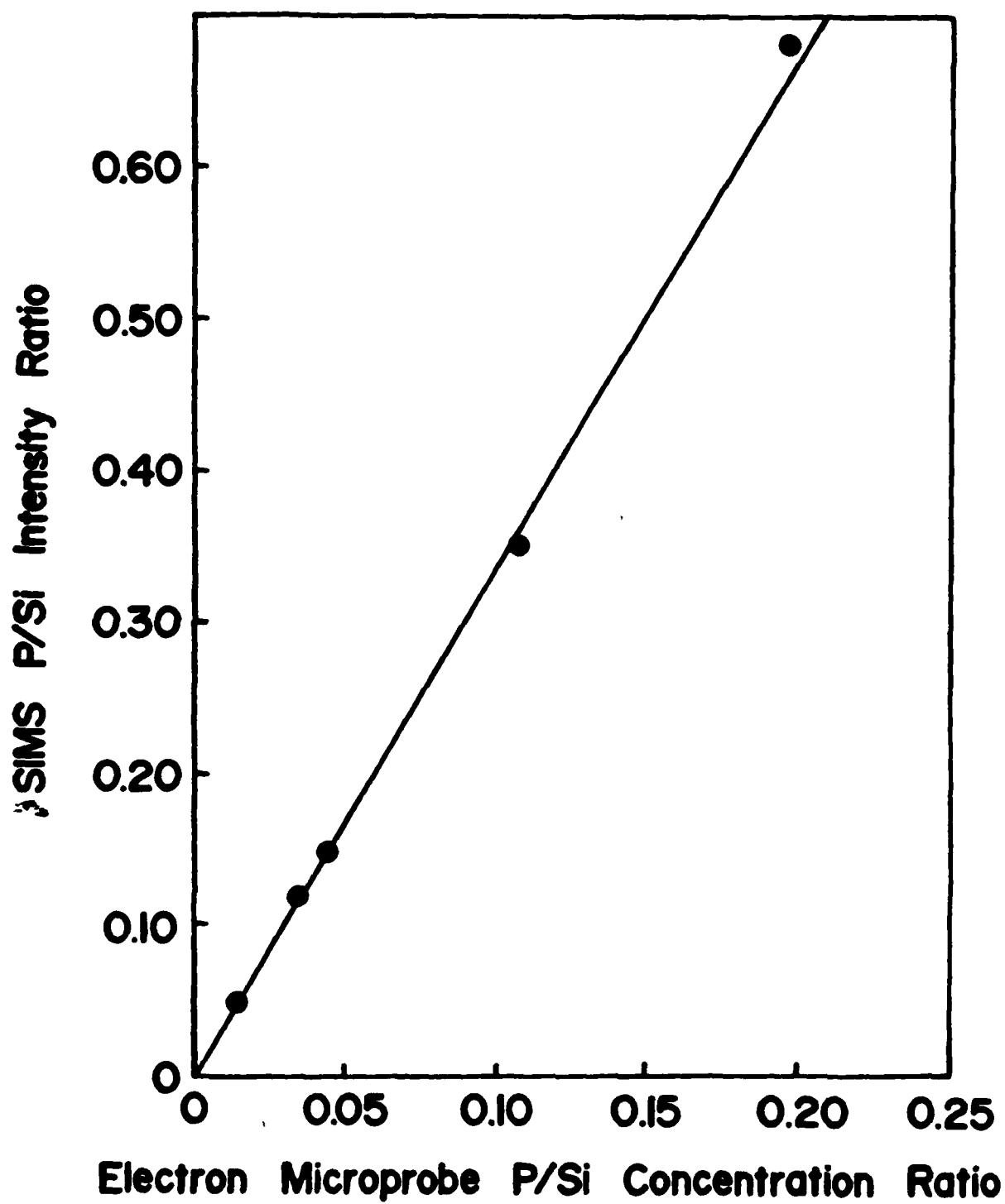


Figure 2

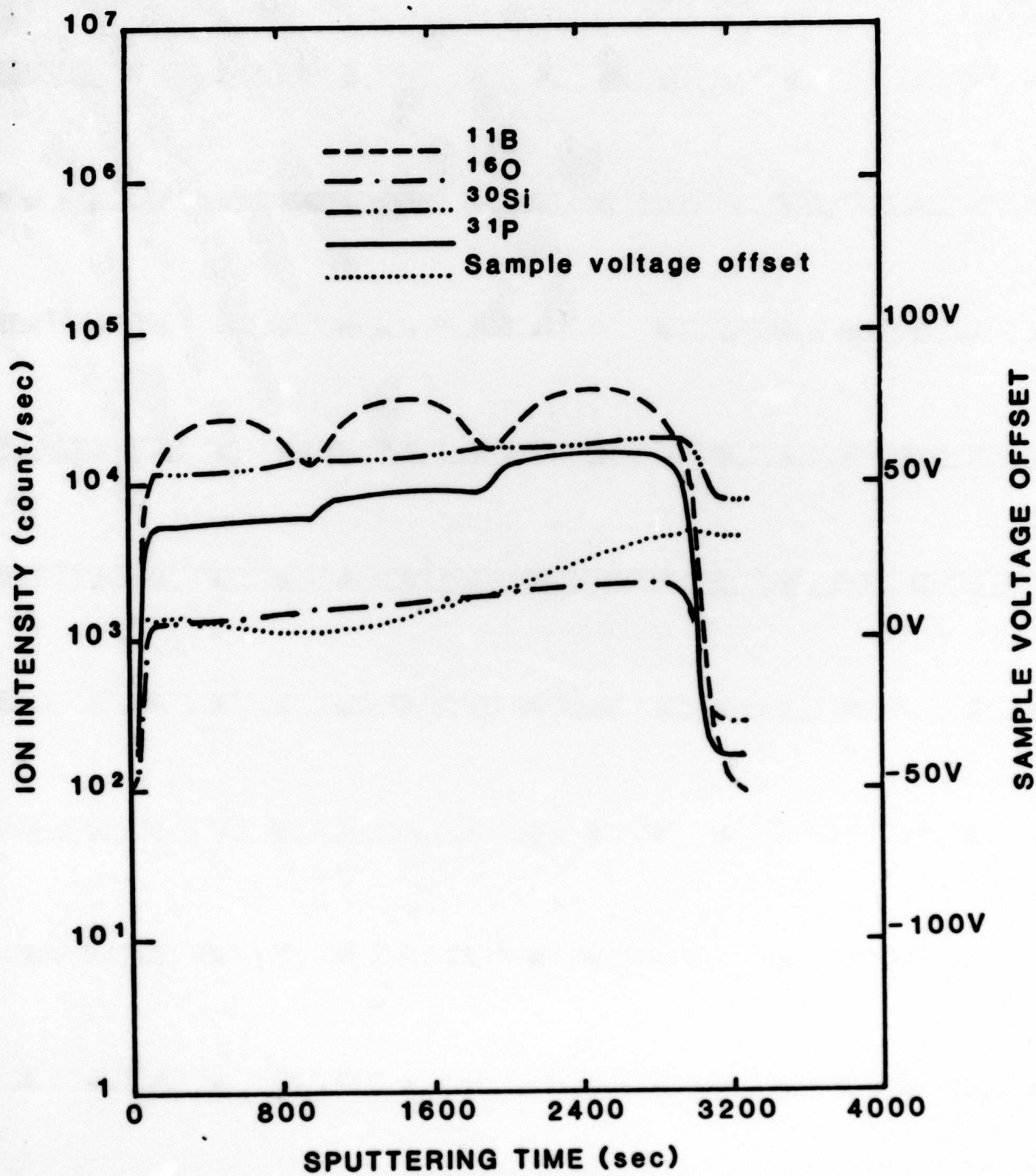
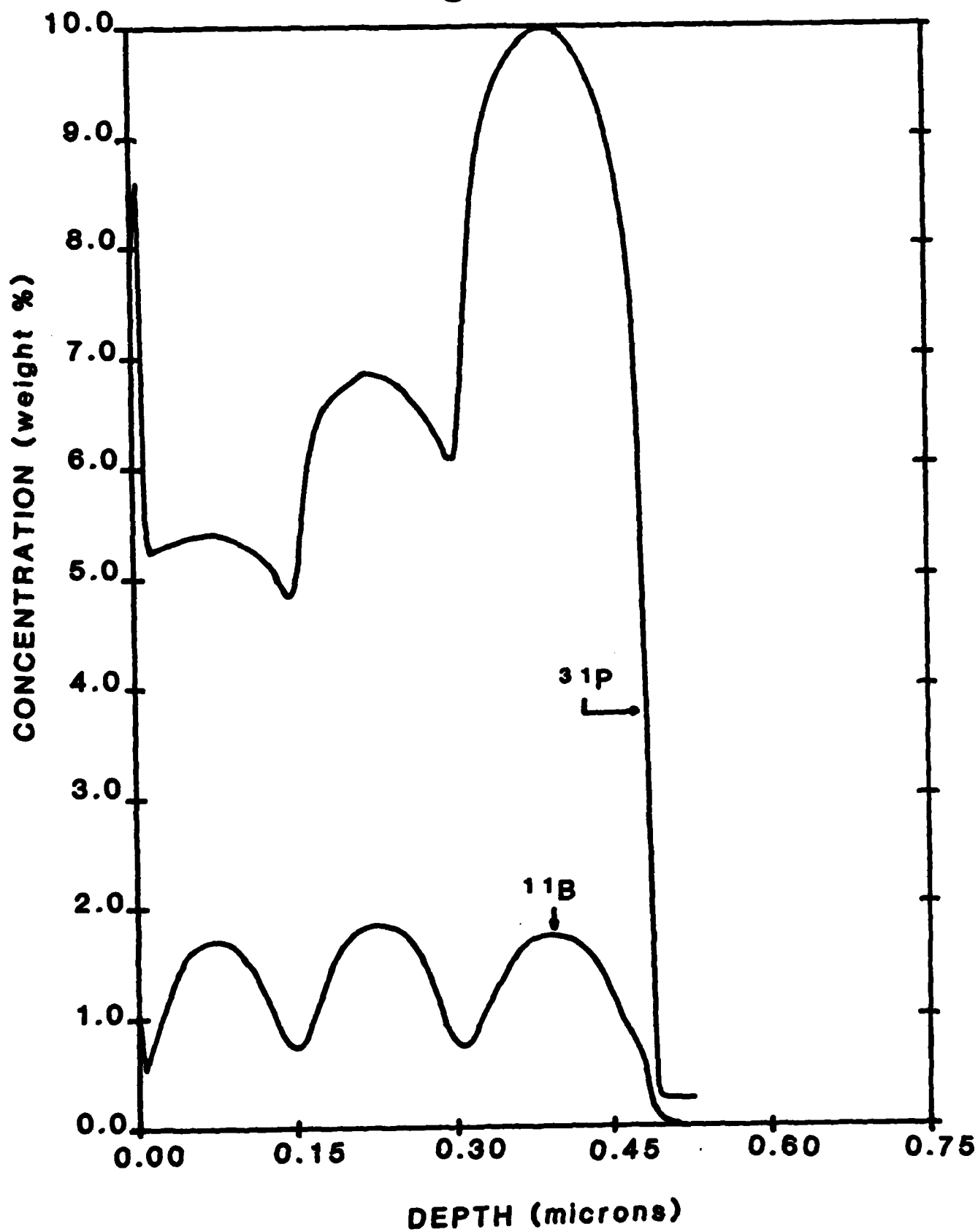


Figure 3

Figure 4



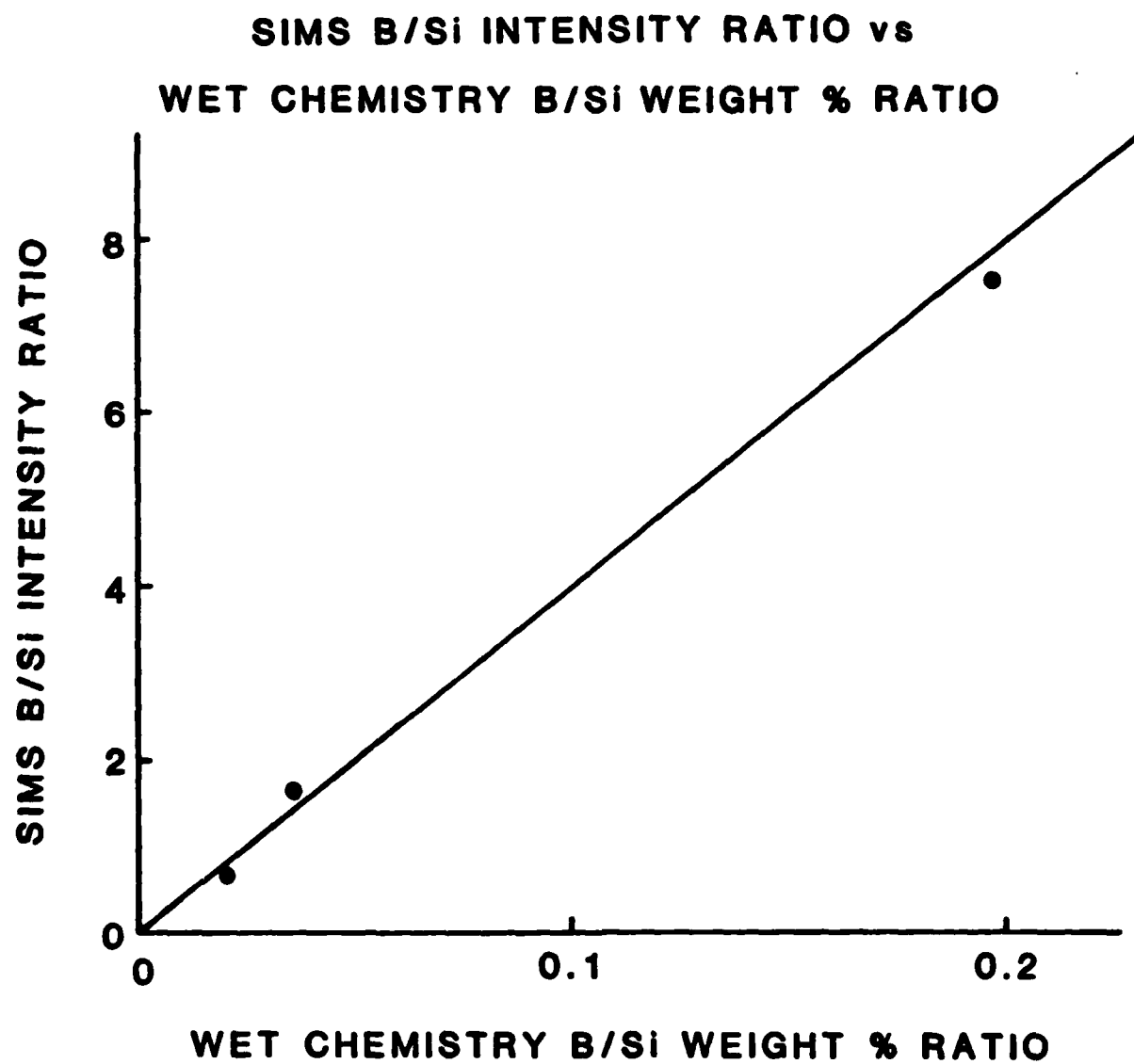


Figure 5

**SIMS P/Si INTENSITY RATIO vs.
WET CHEMISTRY P/Si WEIGHT % RATIO**

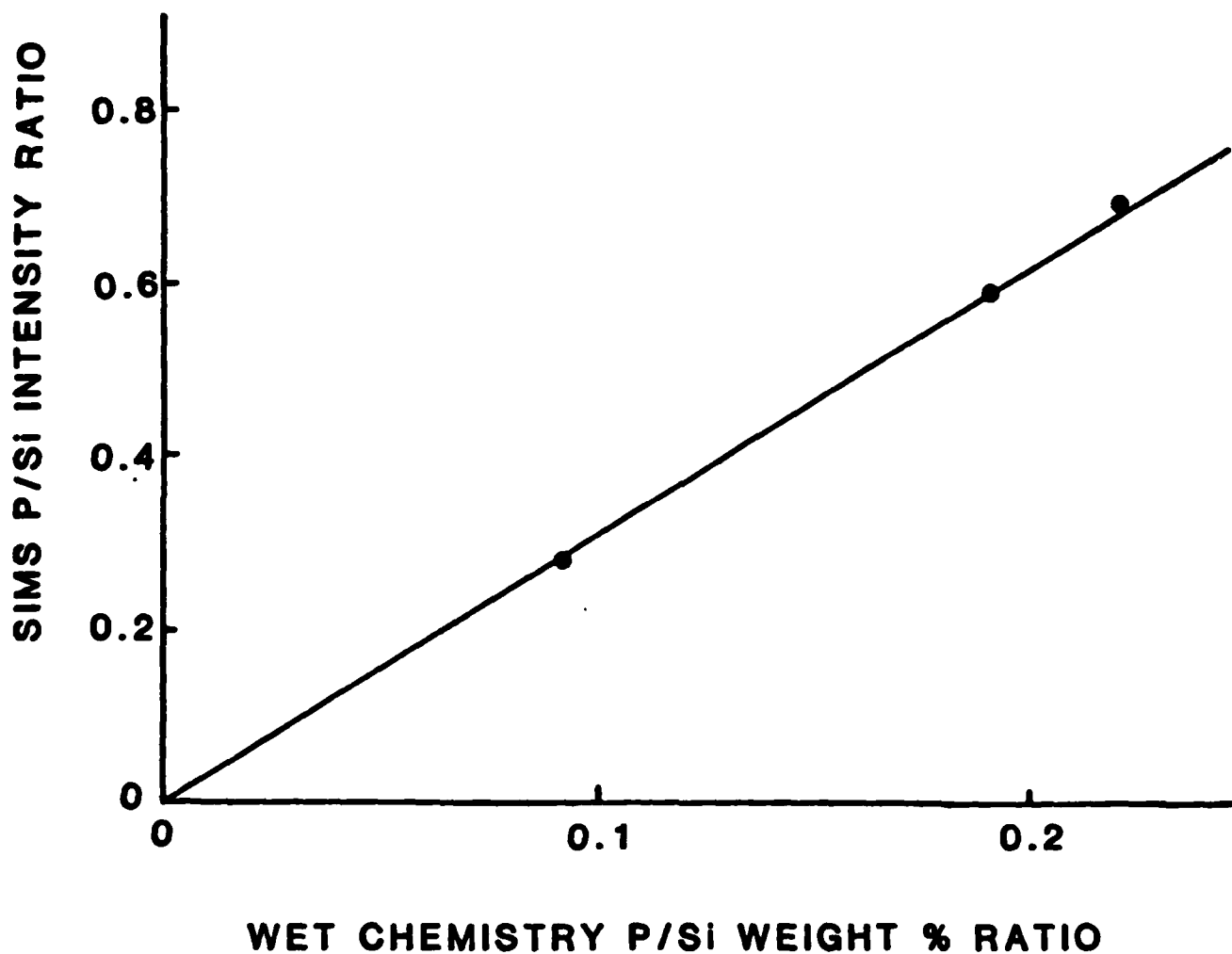


Figure 6

3-STAGE APCVD

O_2
 PH_3
 B_2H_6
 SiH_4

O_2
 PH_3
 B_2H_6
 SiH_4

O_2
 PH_3
 B_2H_6
 SiH_4

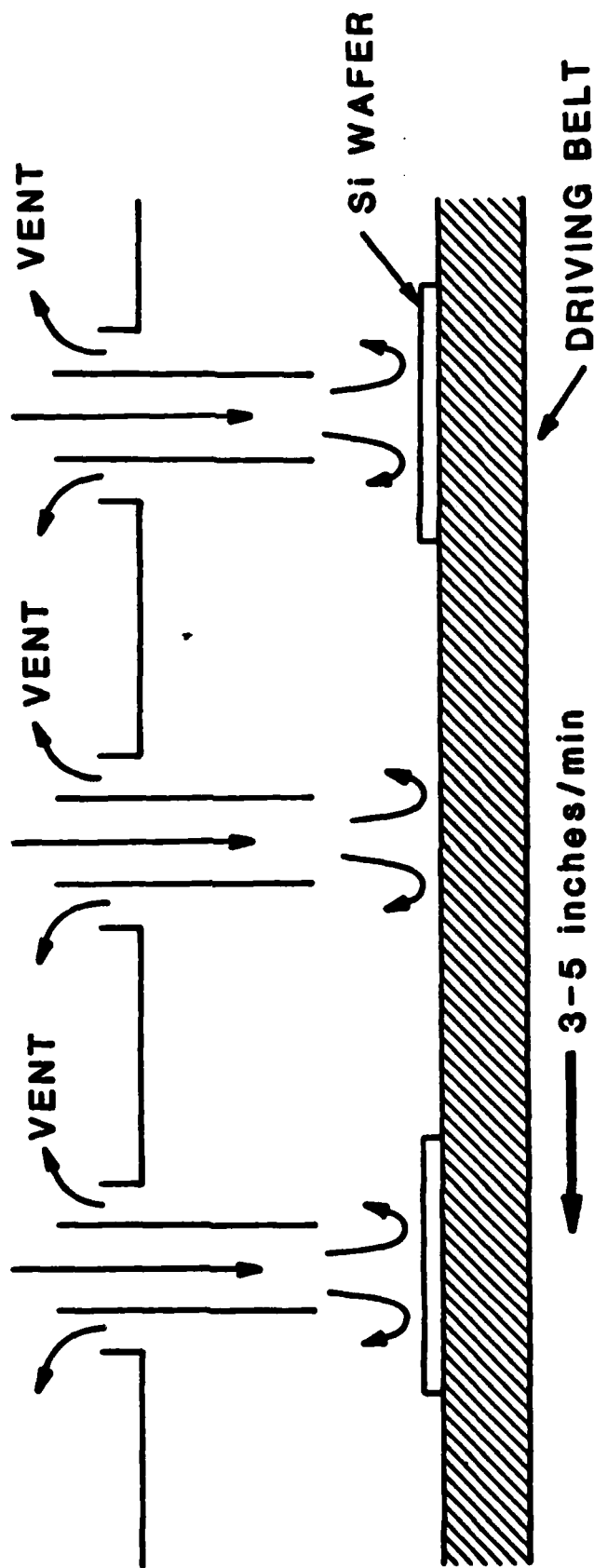


Figure 7